

SCIENCE FOR CERAMIC PRODUCTION

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DEVELOPMENT OF RUGGED AND CRACK-RESISTANT STRUCTURES IN CERAMICS (REVIEW)

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The paper considers methods for increasing crack resistance in ceramics, including microcracking in local stress areas, reorientation of crack movement, polymorphous martensite transition in partly stabilized zirconium dioxide, and bridging of cracks with a plastic phase or crystals with highly nonisometric shape (plates, needles, fibers) in the context of the irreversibility and nonequilibrium, producing self-organization, and a synergetic approach. The possibility of increasing crack resistance due to diffuse polymorphous transitions, twinning, and mechanochemical reactions is discussed.

The desire to develop structures capable of operating in aggressive environments and at high temperatures made design engineers consider ceramics. The specifics of ceramics and, first of all, the brittle nature of their failure, make one search for ways of improving the crack resistance. For this purpose, it is necessary to provide for dissipation of crack energy [1]. In this connection it is necessary to pay the utmost attention to areas of stress concentration; the products should not have sharp angles, nicks, and other defects. The external shape of a product can be considered as an element of its macrostructure of maximum size in a series of other, smaller elements. Thus, the greater the size of grains and crystals, the greater the stresses arising at their boundaries.

In order to provide thfore maximum strength, ceramics must be poreless and finely crystalline. To produce such ceramics, highly disperse powders, additive delaying the growth of crystals, and hot pressing [2] are used. Anisotropy of the coefficient of thermal linear expansion (CTLE) of the crystals combined with their highly non-isometric shape facilitates the emergence of microcracks at their boundaries. Ceramics produced from crystals with highly anisotropic CTLE has low CTLE and low strength due to the existence of microcracks at the boundaries. [3] The greater the size of the crystals, the larger the cracks and the lower the strength. With increasing temperature, the cracks disappear due to expansion

of the crystals and the strength of ceramics produced from anisotropic crystals increases.

It is practically impossible to avoid the emergence of microcracks and other stress concentrators in the course of production of ceramics. Therefore, it is considered more promising to create a structure which impedes the cracks growth, i.e., dissipating to the maximum degree the energy of the crack. The energy of the crack can be dissipated in its frontal zone (apex) or in the planar zone [1]. In the frontal zone, the processes of microcracking, reorientation of the crack and polymorphous transition are the most promising for energy dissipation. In the planar zone, the mechanism of covering the crack with bridges, their plastic deformation, or drawing crystals from the crack walls takes place.

For energy dissipation through microcracking, the apex of a crack has to be in an which that is in a state of stress [4]. In emergence of numerous microcracks, the stress macroconcentrator (the apex) decomposes into numerous microconcentrators, and energy is spent on forming numerous surfaces. It is important that microcracking occurs faster than crack movement in order to be in time to take the energy off the crack apex.

Stress zones appear in ceramics during manufacture due to the difference in the CTLE of neighbouring local areas. In single-phase ceramics, such areas emerge if they consist of crystals with sufficient anisotropy of the cracks [1]. Another method consists in addition to the ceramic matrix of the crystals of a different phase with a slightly higher CTLE: in cooling in the course of firing, these crystals will be in the state of

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stress, and the matrix will be in a state of compression. However, the greater the size of the crystals and the difference between the CTLE of the matrix and the crystals, the greater the probability of emergence of cracks along the boundaries, which usually have lower strength compared to the crystals. If the CTLE of the crystals introduced is lower than the CTLE of the ceramic matrix, stress zones will emerge in the adjacent matrix areas.

It is possible to obtain areas of stress in ceramics at the expense of local compaction in sintering, but it is difficult to preserve them in the process of further firing and subsequent cooling. The duration of the heat treatment and the presence of plasticity in ceramics at high temperatures enable the stresses to relax.

Local changes in the volume are possible in polymorphous transformations. Crystals undergoing polymorphous transitions can be introduced into the ceramic matrix. If the transition in the added crystals is accompanied by a decrease in volume, these crystals will exist in a state of stress, otherwise it will be the matrix. The problem is to select crystals undergoing polymorphous transitions and the matrix material. Too great a change in the volume in the polymorphous transition may result in the appearance of microcracks. The matrix substance should not react chemically to the crystals and chemically stabilize the high-temperature phase. In a transition accompanied by an increase in volume, the matrix can physically stabilize the high-temperature phase and develop compressive stresses which impede the transition. It is possible to avoid the appearance of cracks by selecting the matrix material and mostly by selecting the crystals undergoing the polymorphous transition with a particular change in the volume and having a particular size.

An example of efficient slowing of the crack by microcracking is the introduction of aluminum oxide microspheres into ceramics [5]. If the heat treatment procedure allowed preserving their outer surface in the state of stress, the crack running into a microsphere resulted in its microcracking. The microsphere in the fracture site was covered with a lattice of microcracks. Most often under firing, the stresses in the microsphere relaxed, it was not in a state of stress and in the fracture site broke into two halves. The presence of the stress areas increases the crack resistance but decreases the strength of the ceramics.

Dissipation increases with a change in the orientation of the crack, which requires the presence of sites with a local residual stress effect or sites with weakened boundaries [4]. If a crack selects the least strong site, its length and the total work increase. Such defects as crystal and phase boundaries and microcracks contribute to reorientation of the crack: a crack running into them alters its direction. Defects oriented perpendicularly to the direction of crack movement are the most effective in retarding it. Structures altering crack orientation have high heat resistance, and a whole series of effective techniques have been developed to create them [6]. Reinforcement of the ceramic matrix with disk-shaped particles is

considered the most efficient way [7]. The crack resistance improves with an increase in the ratio between the diameter of the disk and its width. The crack tries to find the least energy-consuming path, but the search takes time. If the crack has accumulated enough energy, it moves so fast that it only has time to react to defects whose orientation most coincides with its own direction. In these conditions, the system passes to long-range action when the crack moves to the opposite side of the sample almost by the shortest direct line.

Reorientation of the crack can occur upon its encounter with the pores that are the structural elements of many kinds of ceramics. A microcrack running into a pore can stop since the radius of the crack apex increases and consequently, stress concentration in the apex decreases. It is preferable that the pore have a spherical shape since independently of the direction of the crack is approach to the pore, it provides the maximum radius for the given volume. If the shape of the pore is far from spherical, its action depends on the direction front which the crack approaches. The presence of sharp angles in the pores causes them to become stress concentrators. The determination of the porosity by water absorption used in ceramics technology cannot provide data on the shape of the pores. In order to determine the shape of the pores and their orientation, it is necessary to analyze parallel slices [8].

The increase in crack resistance through reorientation of the cracks is implemented in ceramic materials with a laminar granular structure [5]. First the films were molded from finely dispersed and coarsely dispersed powders or microspheres of aluminum oxide. The films were assembled in packets and cut into cube-shaped granules. The granules were molded into samples. The structures resulting after firing efficiently dissipate the energy of the crack through its reorientation between the layers and the granules, therefore they have high crack resistance.

A microcrack can be retarded through inclusions of a plastic phase (metal, vitreous phase at elevated temperatures) [1]. The energy of the crack apex is dissipated through plastic deformation. The higher the plasticity of the phase, the sooner the energy is dissipated. If a crack possesses high energy and velocity, i.e., the degree of nonequilibrium of the process is great, the mechanism of energy dissipation through plastic deformation does not have time to function. Then the inclusion material manifests its brittle properties. The crack may cause brittle fracture or bypass the inclusion along the boundary, as was described above for brittle phases. The increase in crack resistance due to brittle fracture through microcracking or reorientation of the crack causes a decrease in the strength of the ceramic. As distinct to it, the introduction of a plastic phase does not decrease the strength of the ceramic at room temperature and may even increase it.

An efficient method of increasing the crack resistance and strength of ceramics is taking the energy off the crack apex through a polymorphous transition with an increase in the volume. This mechanism is implemented in partly stabilized zirconium dioxide (PSZD) [2]. The energy of the crack

apex causes the transition of zirconium dioxide from the metastable tetragonal phase to the stable monoclinal phase with an increase in the volume. The transition occurs in the area immediately surrounding the crack apex. The tensile stresses in the area in front of the crack apex facilitate the polymorphous transition since it is accompanied by an increase in the volume. The expanding area is surrounded by the basic ceramic phase which by tension impedes expansion and produces compressive stress in the emerging monoclinal phase. The crack apex falls into a trap consisting of compressive stresses and is retarded.

The uniqueness of zirconium dioxide consists in the quickness of the action of the crack retardation mechanism. The quickness of this action is due to the fact that the polymorphous transition in PSZD belongs to the martensite type [9]. Unlike many others, it is not a diffusion transition, and it requires insignificant displacement of atoms. Other polymorphous transitions accompanied by an increase in the volume as, for example, α - β cristobalite or β - γ bicalcium silicate, are not diffusion transitions but martensite ones. They are too slow for the rapidly moving crack. This is probably the reason for the absence of data on the successful application of these materials for improvement of crack resistance similar to the one observed in PSZD.

The sensitivity of the polymorphous transition in PSZD is controlled by the quantity of the additive (MgO , Y_2O_3 etc.) stabilizing the tetragonal phase and the size of its crystals. An excessive increase in the sensitivity (instability of the tetragonal phase) causes spontaneous transition to the monoclinal phase with a slight increase in thermal fluctuations. Prevention of spontaneous transition, i.e., preservation of the tetragonal phase, is the main problem in the production of ceramics containing PSZD. Long exposure at a temperature of 200 – 500°C, especially in the presence of water vapor, often resulted in a spontaneous transition and catastrophic loss of strength [2].

The introduction of PSDZ crystals into other types of ceramics effectively increases their strength and crack resistance [2]. The problem consists in excluding chemical reactions with the matrix material which may cause binding of zirconium dioxide in other chemical compounds, destabilization of PSZD, or stabilization of the cubic phase of zirconium dioxide. The concept of using polymorphous transitions in other crystals is related to a whole series of problems. The main problem is the transition rate, which has to be greater than the velocity of the crack. Diffusion transitions are too slow. A transition accompanied by an increase in volume after passing via the crack apex to the planar zone will only contribute to opening of the crack and accelerate its migration. However, it is not inconceivable that if the crack moves slowly as, for example, in tests for long-term strength, the crack energy can be removed.

The twinning of crystals is accompanied by expenditures of energy and can be considered a possible mechanism for dissipating the energy of the crack apex. Some crystals are

capable of forming mechanical twins. They appear when in the result of deformation, two parts of a crystal are found in positions of mirror-symmetry or on in positions turned with respect to the second order axis [10]. Thus, part of the calcite crystal under the effect of mechanical loads passes into the twin position. The twinning system, i.e., the twinning axis or plane depends on the type of crystallographic structure. Twinning results in the emergence of twinning boundaries. Similar phenomena are observed in polycrystalline ceramics [11]. Twinning is possible only in certain kinds of crystals. The twinning process takes time that is not available with fast movement of the crack. In the case of slow movement of the crack, the twinning process could take some energy off the crack.

Theoretically, the energy of the crack apex could be dissipated through mechanochemical reactions. The initial substances could be located between the ceramic components or in the surrounding environment. It is most suitable to take off the energy through endothermic reactions such as reactions of the decomposition of the molecules of the environment or the solid phase deliberately introduced into the ceramic. The release of gas is inadmissible since it would facilitate opening of the crack. However, as in the case of polymorphous transitions, the main problem consists in the low speed of these reactions compared to the speed of crack movement. If the crack moves slowly, these reactions may have enough time to proceed. Note that the chemical interaction with the environment (corrosion) may often accelerate crack movement in long-term strength testing [12]. The chemical reaction between the material and the corrosive facilitates rupture of chemical bonds at the crack apex.

The investigation of retarded fracture of aluminooxide ceramics with a boron silicate vitreous phase showed that this process proceeds in water somewhat more slowly than in air [13]. At the same time, part of the energy at the crack apex is spent on breaking of the chemical bonds in the water and formation of hydroxides at the crack surface. The process is facilitated by relatively low resistance of the boron silicate phase to the action of water. The strength of the samples determined by a catastrophic crack was lower in water than in air. For a rapidly progressing catastrophic crack, the chemical reaction is too slow and does not have time to take energy off the apex. At the same time, water impedes the "healing" of the cracks and increases the probability of emergence of the defects from which the catastrophic crack originates.

There are chemical reactions which proceed at a rate comparable to the rate of crack movement, for example, self-propagating high-temperature synthesis (SHS) [14], but they are highly exothermic. The crack energy could be used to overcome the activation energy of the chemical reaction. However, the intense release of heat in SHS will cause local heat shock, emergence of microcracks and even macrocracks. At the same time, the heat released may result in the emergence of a plastic area in front of the crack apex. Microcracking and alteration of the trajectory, as well as an increase in

plasticity, have good prospects for increasing crack resistance. It is not clear whether these processes will have enough time to proceed before the rapidly moving crack. In the case of slow movement of the crack, its energy may not be sufficient to overcome the reaction activation energy. It is technologically difficult to create inside ceramics areas where the SHS process can take place, therefore the use of this method for improving crack resistance seems highly problematic.

In the planar area, crack movement is retarded by bridging, when bridges are formed between the crack sides. An increase in the distance between the sides (opening) facilitates movement of the crack. Bridging of the crack impedes its opening and slows its movement. The processes in the planar area can proceed much more slowly than at the crack apex, i.e., the energy can dissipate through the lengthier processes. Bridging of the crack can also occur due to inclusion of plastic materials [12]. The emerging bridges are deformed plastically, impeding opening of the crack and dissipating its energy. The plastic phase can be represented by metals and at high temperatures by the vitreous phase. The plastic phase also affects the crack apex, resulting in its retardation, microcracking, and reorientation. Introduction of the metal phase is related to some technological problems, such as the difference of the sintering temperature of the metal and ceramic phases, the possibility of oxidation of the metal, etc.. The presence of the metal phase changes the physicochemical properties of the ceramic material, which is sometime unacceptable.

It is easy to ensure the presence of a vitreous phase in ceramics: it is sufficient to introduce the required additives. At high temperatures, the vitreous phase contributes to blunting of the crack but at the same time increases the propensity to fracture due to cracks growing under a static load (the long-term strength decreases) [4]. Strength tests of samples made of aluminum dioxide with 5 wt.% impurities showed that the strength increases sharply with a decrease in the glass viscosity within the temperature range of 750 – 800°C, and then begins to drop sharply [15]. The higher the loading rate and, consequently the degree of nonequilibrium of the process, the lower the viscosity of the vitreous phase should be in order to give time for plastic deformation to take place. Therefore, the increase in the loading rate shifted the strength maximum to the range of the higher temperatures in which the glass viscosity is lower.

The second method of energy dissipation in the planar zone is bridging of the crack with brittle inclusions of non-isometric shape: needles, plates, threadlike crystals, fiber fragments. Such inclusions affect the crack apex as well, due to mechanical cracking and reorientation of the crack. In the planar zone, the crack energy is spent on elastic deformation of the covering bridges and the work done overcoming the resistance forces in the course of drawing such crystals from the matrix [4]. This is especially evident when threadlike crystals are used [4]. If the crystals are firmly fixed in the matrix, they rupture and the crack resistance increases only

slightly. The greater the loading rate, i.e., the degree of process nonequilibrium, the weaker the bond between the fiber and the matrix must be so that drawing out of the fiber can take place. However, if the crack moves slowly, a weak bond with the matrix facilitates drawing out of the fiber. The strength of the bond between the fiber and the matrix should depend on the degree of nonequilibrium of loading of the product in service. If both rapid and slow growth of cracks are possible, it is advisable to have in the samples fibers with different bonding strength with the matrix.

The introduction of highly non-isometric crystals into ceramics creates a series of technological problems in producing compact samples [2]. In the usual sintering, these inclusions impede shrinkage and, as usual, do not allow obtaining compact samples. In this case, hot pressing is needed, which increases the cost of production. Moreover, since the CTLE in these inclusions differs from that of the matrix and is anisotropic, they can cause the appearance of microcracks in the course of cooling after firing. The inclusions also act as stress concentrators. It is possible to apply special dividing layers on the surface of the crystals before mixing them with the matrix material in order to control the strength of the bonds between the crystal and the matrix [2].

A system (the ceramic sample) always resists an external effect, including mechanisms of energy dissipation. The small elements of the structure unite into larger elements and act consistently, i.e., corporately (synergetically) if this enables them to dissipate the energy more effectively. If the process is spontaneous, the system selects the most efficient way in the given conditions, and usually this is the formation of a catastrophic crack. However, it is possible to create in advance within a ceramic sample a structure capable of dissipating energy through simultaneous formation of a number of microcracks, and then in the given conditions none of these microcracks would become a catastrophic one.

The main types of structural ceramics are brittle materials. Their ideal strength is determined by the strength of the chemical bond and is quite high, but the actual strength is much lower due to the existence of stress concentrators. These are microcracks, pores, crystal and phase boundaries, weakened areas, and local stress areas. Various methods for dissipation of crack energy are used to improve crack resistance. Energy dissipation can be performed through brittle failure or plastic deformation.

In order to dissipate energy through brittle failure, the microcracking or reorientation mechanism is used at the crack apex, and in the planar area the mechanism of bridging the crack with brittle crystals and overcoming resistance forces in drawing these crystals out of the ceramic matrix are used. Microcracking and reorientation of the crack proceed through structural elements which are stress concentrators. i.e., they result in a decrease in the strength. This is especially true when microcracks are used for this purpose in developing a fragmentary structure [6]. If the ceramic item contains no cracks but has weakened areas or local stress areas, the

strength can be increased while high crack resistance is maintained. The strength of ceramics can be further increased by introducing threadlike crystals and fiber fragments. The main advantage of the brittle nature of crack energy dissipation is the ability to preserve high strength up to high temperatures.

For dissipation of crack energy through plastic deformation, the presence of a plastic phase is required in ceramics. The plastic phase can be represented by a metal or at high temperatures by nonmetallic materials such as a vitreous phase. Although the vitreous phase may produce an increase in the strength with an increase in the temperature within a certain temperature range, later on the strength decreases sharply. A metal phase can decrease the chemical resistance of the ceramics. The strength of ceramics with metal inclusions with an increase in the temperature usually declines much faster than that of ceramics with no metal phase. Introduction of a metal phase makes it possible to obtain materials possessing high crack resistance and strength at room temperature.

The improvement of crack resistance due to the polymorphous transition in PSZD has special significance. The crack resistance and strength of such materials are highest among ceramic materials. The crack retardation mechanism functions in terms of brittle failure. With an increase in the temperature, the strength drops sharply, approaching the strength of ceramics based on fully stabilized zirconium dioxide since the mechanism of crack retardation due to the martensite transition stops functioning [2]. It is important to note that the crack retardation owing to the polymorphous transition produces accumulation of tensile stresses in the matrix. At a certain time, this may cause fracture of the sample.

An important role is played by the degree of nonequilibrium of the loading process and the crack movement. The greater the nonequilibrium is, the more evident the brittle properties of the material become, and its strength approaches the ideal strength. The greater the degree of nonequilibrium, the less time the system has for implementing mechanisms of energy dissipation, and they lack enough time to happen. In other words, each process has its relaxation time, and if the time is insufficient, the process does not occur. Different dissipation processes may take place depending on the degree of nonequilibrium. With a high loading rate, the plastic phase behaves as a brittle phase, since plastic deformation requires time. Strengthening and the increase in crack resistance at the expense of the polymorphous transition is implemented only for PSZD since the martensite transition is very rapid.

The increase in crack resistance due to some sufficiently slow chemical reactions has not yet been implemented, although the process of self-propagation high-temperature synthesis appears promising enough. At the same time, it is not inconceivable that in slow propagation of the crack, diffuse polymorphous transitions, twinning, SHS reactions, and mechanochemical reactions of the material with the environment may have enough time to happen. The problem of the degree of nonequilibrium in slow lengthening of the crack re-

mains unclear. It is possible that if the amount of energy released is low, the system may slow this process owing to its inertia, reducing the degree of nonequilibrium. The available data indicate that subcritical growth of a crack in an aggressive environment can proceed in three stages [12, 16, 17]. In the first stage, the process is limited by the speed of the reaction between the material and the corrodent (the aggressive component of the environment) at the crack apex, on the second stage it is limited by the shifting of the corrodent toward the crack apex. The third stage is related to sharp acceleration of crack movement when the chemical reactions at the crack apex do not have time to take off its energy and do not interfere in the process.

The rate of crack propagation results in the fact that the system does not have time to use the mass transfer mechanism to modify its structure. The terms of strength tests differ significantly from the terms of a slower process such as a creep test when the structure tested has time to alter significantly in the course of the process due to mass transfer. The high degree of nonequilibrium (rate of crack propagation) in brittle failure does not allow time for the system to develop new dissipation structures in the course of destruction. Only the structures that had been created in the ceramics in the course of its manufacture can be used by the systems as dissipating structures.

The rate of crack energy dissipation through the structural elements developed in advance within the ceramics have to be faster than the rate of crack movement. Such dissipation at the crack apex is observed when the direction of crack movement changes, when the crack branches upon getting into a stress area, or in the martensite transition. On the crack walls, the mechanism of bridging is active. Bridging of the crack impedes it opening and slows its movement. The reasons for bridging can be friction at the grain boundaries or the presence of crystals of highly nonisometric shape (fibers, threadlike crystals, needle-like crystals, plates) in a ceramic material. The presence of plastic areas in the ceramic, such as, for example, metal inclusions, dissipates the energy through plastic deformation in the frontal zone and bridge energy in the planar zone. All these structures have to be developed in ceramics in advance, since the short time of crack propagation does not give the system time to develop these structures in the course of the process.

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